SCIENCE FOR CERAMIC PRODUCTION

DECORATIVE ZINC-CONTAINING CRYSTALLINE GLAZES FOR ORNAMENTAL CERAMICS (A REVIEW)

N. V. Rudkovskaya[1] and N. Yu. Mikhailenko[1]

Published data on compositions and properties of zinc-containing crystalline glazes for ornamental ceramics are summarized. Current concepts of the mechanism of crystallization and spherulite formation in a glaze coating are discussed, The possibility of controlling the crystallization process and decorative properties of glazes by varying firing conditions and parameters is demonstrated. Examples of production of tinted crystalline glazes are described.

Special attention is currently paid to sophisticated decoration of ornamental ceramics. One of the promising decoration methods is using crystalline glazes. Crystalline glazes are low-melting glasses deposited on a ceramic substrate that partly crystallize under firing and form crystals of various compounds, sizes, and morphology. Microcrystalline glazes contain fine crystals not visible to the naked eye and are opacified (nontransparent). Macrocrystalline glazes containing significantly larger crystals are visible to the naked eye, and their residual vitreous phase can be either clear or opacified.

Crystalline glazes belong to the finest decoration techniques; they impart a refined unique pattern to the surface of ceramic articles [1]. The unique effect is achieved by the fact that inside a clear matrix glaze one can distinguish crystalline formations of various shapes and colors, whose size can reach several millimeters or even centimeters. Zinc-containing crystalline glazes are promising, as they form spherulite and paniculate formations of willemite $2ZnO \cdot SiO_2$ of various colors and sizes shaped like single crystals or crystal clusters [2].

Chemical composition of glazes. The compositions of crystalline zinc-containing glazes as a rule are multicomponent and include SiO_2, Al_2O_3, B_2O_3, ZnO, CaO, MgO, K_2O, Na_2O (Table 1) [3 – 6]. If converted to three components, most compositions belong to the $SiO_2 – ZnO – K_2O$ system.

The main component ensuring crystallization of these glazes is zinc oxide. Furthermore, ZnO decreases the visco-sity and surface tension of the glaze melt, which facilitates spreading of the melt over the substrate and formation of a high-quality glaze coating [7]. The introduction of ZnO also has a favorable effect on the luster and chemical resistance of glaze.

High concentrations of Al_2O_3 have a negative effect on the crystal-formation process; therefore, the weight content of Al_2O_3 in glazes does not exceed 10%.

The content of CaO and especially MgO in glaze compositions has to be restricted, since these oxides increase the surface tension of the melt. Due to this, certain authors recommend a total exclusion of MgO [8].

Alkaline components in crystalline glazes are represented by sodium and potassium oxides. It is established that Na_2O to a greater extent decreases the viscosity of zinc-bearing glazes; however, K_2O provides for lower surface tension ($\sigma_{K_2O} = 0.1$ N/m, $\sigma_{Na_2O} = 1.5$ N/m) [9]. Therefore, in some cases the introduction of K_2O in the glaze composition is preferable.

To decrease the viscosity and surface tension, one can introduce B_2O_3 into glaze composition, which is frequently used as a flux in various types of glazes and enamels. The total content of alkalis in high-boron glazes can be decreased, The total content of alkaline components and boron oxide ($\Sigma R_2O + B_2O_3$) and the ratio $\Sigma R_2O/B_2O_3$ determine the firing temperature and other technological properties of glaze (viscosity, surface tension, TCLE).

Mechanism of crystallization of glaze coatings. The formation of crystalline glaze coatings occurs as a consequence of complex physicochemical transformations. On firing at high temperatures, the processes occurring in the frit

[1] Gusevskii Glass College, Gus-Khrustalny, Russia; D. I. Mendeleev Russian Chemical Engineering University, Moscow, Russia.

TABLE 1

Composition	Mass content, %												Maximum firing temperature, °C
	SiO$_2$	Al$_2$O$_3$	CaO	MgO	K$_2$O	Na$_2$O	ZnO	BaO	Fe$_2$O$_3$	TiO$_2$	B$_2$O$_3$	P$_2$O$_5$	
1	46.28	8.22	0.44	–	2.72	2.57	12.12	–	0.41	–	27.24	–	1200 – 1250
2	27.77	4.94	0.26	–	1.63	1.58	36.32	–	0.24	–	27.24	–	1200 – 1250
3	48.43	0.98	6.12	0.66	6.60	5.44	23.20	0.23	0.08	–	8.40	–	1150 – 1200
4	46.89	0.81	7.02	0.36	7.63	4.77	22.31	–	0.04	–	9.90	0.24 CoO	1150 – 1200
5	54.80	0.92	2.74	1.01	2.91	4.36	25.00	0.05	0.35	0.03	–	0.01	1200 – 1280
6	49.42	7.97	4.05	1.94	1.33	7.48	25.56	0.11	0.32	–	3.08 MnO	0.02	1200 – 1280
7	44.19	5.73	4.90	2.78	5.64	4.31	25.50	0.04	0.18	–	1.00 NiO	0.01	1200 – 1250
8	55.17	8.79	3.98	2.56	1.75	7.44	24.92	–	0.29	0.03	1.00 NiO	–	1250 – 1300
9	55.40	6.00	3.10	2.40	2.30	5.55	25.00	–	0.20	–	–	–	1250 – 1320
10	47.80	–	–	–	14.60	1.90	30.60	5.10	–	–	–	–	1250 – 1300
11	44.20	6.80	2.30	–	10.0	1.20	21.10	3.40	–	8.00	–	3.00 ZrO$_2$	1250 – 1300
12	49.10	9.20	3.50	–	5.60	1.90	19.80	8.30	–	2.60	–	–	1150 – 1200
13	44.26	9.06	1.30	–	6.51	2.00	32.34	4.00	–	0.53	–	–	1250 – 1300
14	49.17	9.61	3.26	–	6.15	1.90	20.90	9.03	–	–	–	–	1250 – 1300
15	69.80	4.47	–	–	1.66	5.75	8.00	–	–	7.01	3.33	–	1250 – 1300
16	55.85	3.57	–	–	1.34	4.60	25.01	–	–	7.00	2.64	–	1250 – 1300
17	41.50	–	4.90	–	–	8.40	31.60	–	–	–	13.60	–	1200 – 1250

layer deposited on the ceramic substrate first result in the formation of a thin vitreous glaze layer and then lead to partial crystallization of this layer.

A glaze layer is formed as a result of spreading of a vitreous melt over the substrate surface and the physicochemical reactions of this melt with the ceramic substrate. The reactions between the glaze and the ceramic may include diffusion of cations, mass transfer by means of a viscous glaze melt flow and softening of the vitreous phase of the ceramic, chemical reactions between the melt and the crystalline phases of the ceramics, and formation of new compounds in the transition layer [1, 2, 10]. These processes are observed in the formation of both transparent (noncrystallizing) glazes and crystalline glazes.

The crystallization of zinc-containing glazes is a particular case of crystallization of glass-forming melts and obeys the general laws of crystallization of melts and glasses. It is known that the crystallizing capacity of a melt is determined by two factors:

– spontaneous or deliberate formation of crystallization centers (seed formation), which is quantitatively characterized by the number of crystal seeds N arising in unit volume per unit time under a certain degree of overcooling;

– crystallization rate v, which is understood as the average rate of crystal growth.

Both factors depend on temperature (or degree of overcooling) of the melt. The temperature dependences of seed formation $N = f(T)$ and the crystal growth rate $v = f(T)$ have typical maxima at temperatures T_I and T_{II}, which correlate with the formation of a maximum number of seeds N_{max} and a maximum rate of crystal growth v_{max}. The most favorable conditions for the fullest possible crystallization of the melt are implemented within the temperature interval between these maxima [11].

The kinetics of the processes of seed formation and growth of willemite crystals in a zinc-bearing glaze were first studied in sufficient detail by Norton [12]. This study determined the quantity and maximum sizes of crystals formed under different firing conditions, and represented experimental temperature dependences of the seed formation rate and the crystal growth rate. The author stressed that to avoid dullness in glazes and to obtain large spherulites, it is necessary to heat the glaze to a sufficiently high temperature (the spread temperature), at which the majority of the crystallization centers present in the melt are dissolved, and then bring the temperature down to the crystal growth temperature and expose the glaze for 0.5 – 1 h at this level.

Subsequent researchers [3 – 5] also stressed the role of firing temperature conditions in the production of crystalline glazes. Indeed, by varying firing and chilling conditions, it is possible to create conditions for the formation of a maximum number of small-size crystals uniformly distributed in the volume of the coating (opacified glazes) or, on the contrary, a limited number of large crystals (crystalline glazes). Experimental confirmations are supplied in several studies of Wanie [13] dedicated to crystalline glazes. The author notes that the mechanism of crystal formation in crystalline glazes is similar to the opacification mechanism, but the number of crystals arising in crystalline glazes is smaller, and their sizes are significantly larger than in opacified glazes.

Zinc-containing glazes are the most interesting with respect obtaining various decorative effects by varying time/temperature conditions for firing of coatings. Zinc oxide in a melt forms compounds with silicic acid and other components, which in cooling form picturesque formations with fluffed-up crystals resembling rosettes. The concentration of ZnO has a great importance, since, on the one hand, ZnO can act as opacifier and lead to the formation of an opaque glaze, and on the other hand, in the case of a too high

TABLE 2

Regime	Glaze spreading (stage 1)	Seed formation (stage 2)	Crystal growth (stage 3)	Visual evaluation of coatings
One-stage	1250 – 1300°C, 10 – 30 min	–	–	Signs of crystallization are absent
Two-stage	1250 – 1300°C, 10 – 30 min	–	980 – 1160°C, 30 – 120 min	Spherulite formations 2 – 12 mm in diameter in the amount of 30 – 400 pieces/dm^2
Three-stage	1250 – 1300°C, 10 – 30 min	700 – 800°C 800 – 900°C 900 – 950°C 950 – 1000°C	980 – 1160°C, 30 – 120 min	Opacified Fine-crystalline structure Spherulite aggregates Isolated spherulites

concentration, it can cause a complete crystallization of the silicate phase.

According to the results of mineralogical and x-ray studies, zinc-bearing glazes contain crystalline formations of two types: fine-crystalline zinc aluminate (gahnite) $ZnO \cdot Al_2O_3$, which acts as an opacifying agent in these glazes, and large-crystalline zinc silicate (willemite) $2ZnO \cdot SiO_2$, which imparts a special decorative effect to the glaze. Whereas the size of gahnite crystals is around 1 μm, the size of willemite crystals reaches 30 – 80 μm, and in some cases significantly more. Occasionally, other phases as well, for instance rutile TiO_2, are crystallized in small quantities.

The morphology of willemite crystals varies significantly depending on the crystal growth temperature (T_{II}). By using different firing temperatures, it is possible to obtain isolated acicular crystals (1160 – 1190°C), two-leaf spherulite formations (1100 – 1160°C), or round spherulites (980 – 1100°C) of willemite in a glaze coating [14]. It is known that these crystalline formations are generically related to each other. Thus, a two-leaf spherulite arises as the cause of splitting of monocrystals and represents a transitory underdeveloped form of a round spherulite [15]. The different morphology of crystals in a glaze coating is often determined by different conditions of their growth, i.e., different degrees of supercooling and different viscosity of glaze melts. Under high temperatures, a glaze melt is less supercooled and less viscous. Such conditions do not contribute to splitting of monocrystals and, accordingly, acicular aggregates are formed. As the temperature decreases, the degree of supercooling and the viscosity of the melt increase; consequently, monocrystals split with formation of two-leaf spherulites. Within the low-temperature range, monocrystals due to a high degree of supercooling and greater viscosity of the melt have enough time to split more perfectly, which leads to the formation of round spherulites.

Willemite spherulites are complex polycrystalline aggregates with a radial structure consisting of well-visible single filament crystals. A specific feature of these spherulites is their two-dimensionality (a flat spherulite) determined by the fact that spherulite formation proceeds in a thin glaze layer (200 – 300 μm). Crystals at the edge of a spherulite are considerably shorter and more chaotically arranged than crystals existing near the spherulite center. Crystals that are located closer to the center in the course of the spherulite growth. i.e., during the migration of the crystallization front, can become elongated, more ordered, and transform into more equilibrium and stable forms [16, 17].

The above specifics of spherulite formation in willemite are presumably determined by the filament-needle structure of these crystals.

Glaze firing conditions. Crystalline zinc-containing glazes are high-temperature glazes fired at 1150 – 1300°C. The temperature-time firing conditions play an extremely significant role in glaze technology and determined the nature of crystallization of these glazes. The development of firing conditions and optimization of their parameters is based on the above-described theoretical concepts of the processes of glaze layer formation and the mechanism of crystal formation in this layer.

Firing conditions in practice should provide for all stages of coating formation: the formation of a vitreous glaze layer and crystal seeds in it, and controlled growth of crystals in the main phase. Since the temperature intervals of these stages do not coincide, the firing regime should be stepwise. The most common is a two-stage regime [3, 4, 18]:

– heating up to the glaze spreading temperature T_s and exposure τ_s at this temperature up to full spreading;

– cooling to the crystallization temperature T_{II} and exposure τ_{II} at this temperature up to growth of the crystals to a preset size.

In this firing regime, the role of crystallization centers is implemented by microparticles and microscopic fluctuations not dissolved in glaze melting.

Sometimes, a three-stage regime is used in glaze firing, in which the glaze spreading stage is followed by cooling of the glaze to the seed-forming temperature T_I and exposure τ_I at this temperature to develop crystallization centers. As a rule, T_I is close to the glaze vitrification temperature T_g. After this stage the glaze is heated up to the crystallization temperature T_{II} and subjected to a respective exposure at the given temperature.

A comprehensive study of the effect of firing conditions and temperature/time parameters on the crystallization and decoration effect of zinc-containing willemite glazes was carried out in [14, 19]. The results of the research (Table 2) [14] indicate that varying the glaze firing regime makes it

possible to control the crystallization process and to obtain glazes with various decorative effects, from opacified to large-crystalline glazes with well-formed spherulites. Furthermore, even a slight variation in the temperature/time parameters in narrow intervals leads to a significant alteration in the quantity and the size of emerging crystals.

Sometimes, high-melting additives acting as forced crystallization centers are added to the composition of crystalline glazes for the purpose of controlling the seed formation process.

Crystalline willemite grains or zinc oxide grains can be used as such additives in willemite glazes. In this case, to prevent too intense spherulite formation, the temperature/time parameters of firing should be corrected toward increasing the glaze spread temperature and crystallization temperature.

Tinting of glazes. To extend the color range of glazes, they can be tinted using traditional pigments: CoO, NiO, CuO, MnO, Cr_2O_3, Fe_2O_3, etc. The introduction of pigments does not have a significant effect on the shape, size, and quantity of crystals formed in firing, and imparts additional ornamental qualities to articles.

The saturation of glaze tint depends on the weight content of the colorants and varies from 0.5 to 3.0%. The color tone of the vitreous matrix and the emerging crystals is determined by the type of the pigment and its valence-coordination state. It the state of the colorant chromophore ion in the glass and in the crystalline phase is the same, the tints of the crystals and the surrounding vitreous phase in the glaze differ only in color intensity (CoO — blue, CuO — green, MnO — brown, and Fe_2O_3 — yellow-brown). The most original are glazes tinted by ions capable of easily changing their coordination state. Thus, a willemite glaze in the presence of NiO acquires a multicolor tint: the spherulites have a bright blue color due to the four-coordination Ni^{2+} cations incorporated in the crystalline structure of willemite, and the surrounding vitreous phase is yellow due to Ni^{2+} cations in six coordination [14].

In firing of tinted glazes it is necessary to maintain oxidizing or neutral conditions, since in a reducing medium, the colorants become partly or fully reduced to their metallic state.

Thus, zinc-containing crystalline glazes are distinguished by refined beauty, originality, and a great variety of decorative effects, which makes them very promising for producing ornamental ceramics.

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